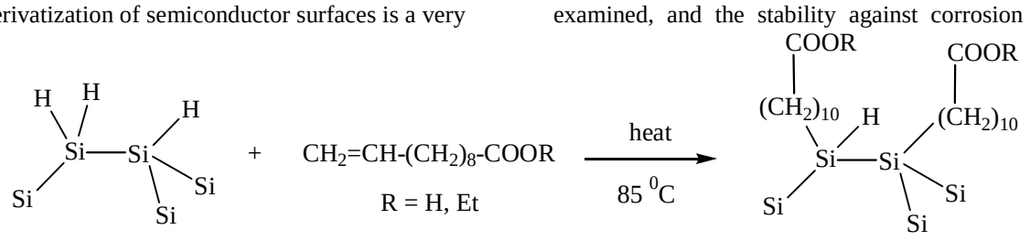
Stability Enhancement of Modified Porous Silicon Nanostructures

R. Boukherroub,[†] D.D.M. Wayner,[†] D.J. Lockwood,[‡] and L.T. Canham[§]
[†]Steacie Institute for Molecular Sciences
[‡]Institute for Microstructural Sciences
National Research Council, Ottawa, Canada K1A 0R6
[§]DERA, Malvern, Worcs. WR14 3PS, UK

Organic derivatization of semiconductor surfaces is a very active field of research because of the role of these materials in modern technology. Controlling the electronic properties and understanding the reactions at the surface of silicon is crucial for developing new devices. Several methods have been proposed in the literature for chemical modification of both single crystal silicon and porous silicon (PSi) surfaces under various conditions.[1-5] Porous silicon is of particular interest following the first report on its bright photoluminescence (PL) at room temperature, as a result of quantum confinement within the nanostructures composing this material.[6] A significant volume of work has been devoted to studying its properties ranging from fundamental aspects of its formation to device applications.[7,8] The most sought after applications so far are based on using the PSi layers for integration into optoelectronic devices. Potential applications based on electrical and/or optical measurements for sensing chemical and biochemical species have been demonstrated using PSi.[9] Recently, an important step towards utilization of PSi for biomedical applications has been achieved. Canham et al. have shown that PSi layers of low porosity are active in vivo and that hydroxyapatite could be grown on the PSi matrix.[10-11]



PSi surfaces are prepared in HF-based solutions by electrochemical or chemical etching.[7] The as-prepared PSi surface is terminated by Si-H_x bonds. This monolayer slowly reacts in air to form an oxide sub-monolayer. For some applications, the PSi matrix is deliberately oxidized in order to achieve a higher stability and better passivation. Oxidation either under thermal, chemical or electrochemical conditions is the most studied route for surface passivation.[12] The oxidation reaction offers some advantages regarding the electronic and chemical stability, but presents some disadvantages associated with the PL of the PSi surface. The oxide related PL is always red independently of the starting porosity, and in the case of samples oxidized thermally, the nanostructure matrix is consumed by the process and only some crystallites remain in the oxide layer, which can affect the PL yield.

This paper describes a chemical route for organic functionalization of PSi layers using undecylenic acid and ethyl undecylenate (see scheme above). In both cases, the hydrosilylation takes place without sacrificing the functional group. Under thermal conditions, alcohols break the Si-Si back bonds of the PSi matrix.[13] In contrast the acid function does not react with either the Si-H or the Si-Si bonds of the PSi surface. The presence of traces of water in the ethyl undecylenate induces, in a competitive process with the hydrosilylation reaction, a partial oxidation of the PSi surface. If the traces of water were removed by adding 5% volume of chlorotrimethylsilane (TMSCl), an oxide free surface can be prepared. The presence of oxide on the surface along with organic molecules offers novel properties to the surface. The surfaces have been characterized using transmission Fourier-transform infrared (FT-IR) and X-ray photoelectron spectroscopies. The effect of the surface composition on the photoluminescence (PL) was examined, and the stability against corrosion in 100% humidity was studied using chemography.

We show that organic functionalization of PSi surfaces under thermal conditions offers an excellent method for the surface passivation and PL preservation of PSi. This route is easy to carry out and is tolerant of different functional groups, which allow further chemical manipulations to achieve more complex structures on the surface. The surface is protected against corrosion when exposed to 100% humidity in air. The presence of small amounts of oxide formed during the chemical process, when no special precautions were taken in order to eliminate the traces of water present in the chemical reagent, increases remarkably the surface resistance against corrosion. The stability of the surface to hydrolysis is, in this case, comparable to that of thermally oxidized PSi surfaces in which the nanostructure matrix is affected by the thermal oxidation process. Such a high surface stability augers well for biomedical applications. The presence of regions of different chemical composition (oxidized regions and organic modified regions) on the surface is of interest for controlling the wetting properties of the surface. This is an important step towards applications of the PSi matrix for DNA and protein microarray processing.

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